

FINAL REPORT-SUMMARY OF RESEARCH
 NASA Grant No. NAG 5-4642
 Washington University Fund #1041-59242

TITLE: Raman Spectrometer for Surface Identification of Minerals and Organic Compounds on Silicate Planets and Small Solar-System Bodies

PRINCIPAL INVESTIGATOR: Larry A. Haskin
 Department of Earth & Planetary Sciences
 Campus Box 1169
 Washington University
 One Brookings Drive
 St. Louis, MO 63130-4899

PERIOD COVERED BY THIS REPORT: July 1, 1997 – June 30, 2000

SUMMARY

This summary is the final report of work on two-year grant NAG 5-4642 (actually the second and third years plus an extension of a three-year PIDDP grant that was initially issued as NAGW-5207). Our objectives for this project were (1) to demonstrate that Raman spectroscopy is an excellent method for determining mineralogy on the surface of the Moon, Mars, and other planetary bodies; (2) to construct a prototype of a small Raman spectrometer of the kind we suggest could be used on a lander or rover; and (3) to test the ability of that spectrometer to identify minerals and quantify mineral proportions in lunar materials and complex Martian analog materials, and to identify organic matter in planetary surface materials, all under roughly simulated field conditions. These goals have been met. The principal accomplishments of this PIDDP project have been the following:

1) Selection for flight. The most important outcome of this project was the selection of our proposed Raman spectrometer, based on the breadboard produced by this project, for the Athena instrument package on the Mars Surveyor 2001 mission. Thus, we achieved (temporarily) the highest goal of the PIDDP program, selection for flight. The 2001 mission was postponed to 2003 because the rover could not be made ready for a 2001 launch. It was later scrubbed entirely as a consequence of the recent failure of the Mars Polar Lander. The mission has now been reconstituted, albeit with smaller rovers, as the Mars Exploration Rover (MER) missions of 2003. Unfortunately, the Raman instrument was omitted from the JPL proposal that led to those missions. We believe this omission was based largely on perceived risk associated with an instrument that had not yet achieved the Engineering Model stage of development, even though the instrument was on schedule approaching that milestone. On behalf of the MER P.I. (Steve Squyres) and ourselves, we presented the scientifically very strong case for inclusion of the Raman instrument as soon as the MER missions had been selected to fly in 2003, and we showed how it could readily be accommodated on the rover. Although it was agreed that our plan was feasible, our petition for inclusion on the missions was turned down. The reasons given were too low margins of mass and volume (even though the mass we needed was <10% of the existing contingency, and we showed how we could fit our instrument outside of the crowded rover WEB). In short, the good news is that this PIDDP instrument was selected for a mission. The bad news is that it cannot fly until a later mission (2007?).

2) Construction of a breadboard Raman probe. We now describe accomplishments in a more chronological sequence of events. Initially, we constructed a breadboard version of the probe of the proposed Mars Raman spectrometer. We did not miniaturize the breadboard fully, but used components that could readily be miniaturized. This included a diode laser, which we knew would soon become available in a new form (DFB, distributed Bragg reflector) and which would provide the wavelength

stability we needed for a flight instrument without stringent temperature control. We tested this breadboard version using the spectrograph of a Raman spectrometer at nearby Monsanto. This resulted in a publication (Wang et al, 1997).

3) Throughput confirmation of the breadboard Raman probe. The DFB laser indeed became available with a wavelength (664 nm) we deemed suitable for good Raman work. As a laser, it worked very well, showing excellent wavelength stability and a very low temperature coefficient of wavelength change. We incorporated it into our Wash U breadboard. In the meantime, our research group acquired a modern laboratory Raman spectrometer system (Kaiser Hololab), purchased by the University. Using the Kaiser spectrograph, we successfully tested the breadboard probe with the DFB laser. The basic throughput of the probe was 77% that of the high-quality commercial probe we used as a standard, the Kaiser Hololab probe, as determined for spectral peaks of five light-colored mineral specimens (calcite, quartz, feldspar, olivine, and sulfur). This matched our expectations. Of these minerals, one (feldspar) gave a relatively low throughput, 33%; the average for the other four is 88%. This is certainly adequate throughput for on-surface Mars work.

4) Selection of a laser. Notice that in the previous section, the values for throughput are based on only light-colored minerals (the olivine specimen was a peridot, not a typical dark olivine). The throughput of the probe is, of course, the same for light of all Raman wavelengths. The Raman scattering intensity achieved for dark minerals by using the 664 nm DFB laser was, unfortunately, anomalously low (<33% of the expected value). This, coupled with the low intrinsic efficiency of the CCD detector for the reddest Raman-scattered radiation from a red laser, meant an unsatisfactory overall performance for the probe. This was a major surprise, and getting such surprises early is part of the reason for the PIDDP program. It was particularly a surprise because, unlike the wavelength 664 nm, the previously tested He-Ne laser wavelength of 633 nm does not give anomalously low results for light or dark minerals relative to a green wavelength of 532 nm once the λ^{-4} dependence is taken into account.

We had chosen the DFB diode lasers for their low power consumption and stability. These lasers were, in fact, the only reasonable choices at the time the breadboard was first constructed. Unfortunately, DFB lasers with wavelengths shorter than 664 nm are not available. Within the past two years, however, small, low-power-consumption, diode-pumped, frequency-doubled YAG-type lasers with an output at 532 nm have become available. We have thus switched the breadboard probe to that wavelength. The green wavelength is a better choice than the red anyway, for two reasons: The intrinsic cross section for Raman scattering of 532 nm green light is 2.5 times stronger than that of 664 nm red light (if the red light had not given erroneously low scattering; it is actually stronger still), and it produces Raman-scattered light in a wavelength that lies in the most sensitive range of common CCD detectors, unlike Raman-scattered red light.

4) A breadboard spectrograph based on our PIDDP design. For two reasons, we did not fabricate a breadboard spectrograph as planned. First, the acquisition of the Kaiser Hololab system (purchased by the University) meant that we could test our breadboard probe thoroughly against a spectrograph of known characteristics. Second, a breadboard spectrograph produced at JPL and based on our design came on line midway during the course of this grant. It had the optical and grating characteristics we had specified, so we chose to test it just as we would have tested a less sophisticated breadboard of our own manufacture. It did not seem productive to produce a less miniaturized breadboard ourselves. We chose instead to concentrate more of our effort than originally intended on the characteristics of the probe. We coupled it with both the Kaiser spectrograph and the JPL breadboard spectrograph.

We had determined the throughput of the Wash U breadboard relative to the commercial Kaiser Hololab probe from testing it using the Kaiser spectrograph. Using the known throughput of the breadboard probe, we were able to test the throughput and sensitivity of the breadboard spectrograph. The spectral resolution was 9 cm^{-1} , close to the design specification of 7.7 cm^{-1} and was slit limited ($50 \mu\text{m}$ slit). The spectrum of a mercury light source is shown in Figure 1, both as it appeared on the grating image and as a CCD trace. This shows the dual blaze character of the grating. This dual blaze provides the spectral range necessary to observe reduced carbonaceous materials such as kerogen-like hydrocarbons, PAHs, and graphite, and bound H_2O and OH. These last were only poorly observed until

the change from red to green for the laser exciting wavelength was made, owing mainly to the low sensitivity of the CCD for the infrared wavelengths of the Raman scattered light from those materials. Figure 2 shows on an expanded scale the splitting of the Hg doublet near 840 cm^{-1} (mercury lamp) and the olivine doublet just above 800 cm^{-1} (as the example of an important mineral). The throughput of the spectrograph was only about 6%, less than the expected 9%. Some of the unexpected signal loss occurred at connectors where signal loss should have been minimal, and this is easily fixed. Much of the rest occurs because of poor slit alignment with the optical fiber that transfers the Raman signal from the probe to the spectrograph. Improvement of these two components will produce a spectrograph with at least half of the sensitivity of the Kaiser Hololab spectrograph.

5) Overall result. Thus, overall, the design for both the probe and the spectrograph is sound, and a flight instrument approaching laboratory quality in resolution and sensitivity can be built. Figure 3 shows spectra taken with the JPL breadboard BB1d coupled to the JPL spectrograph (the overall miniaturized breadboard system based on the design worked out in this PIDDP project). This PIDDP grant provided partial support for 3 papers and 16 abstracts. They are listed below.

PUBLICATIONS

Refereed papers published with partial support by this grant

Haskin L. A., Wang A., Rockow K. M., Jolliff B. L., Korotev R. L., and Viskupic K. M. (1997) Raman spectroscopy for mineral identification and quantification for in-situ planetary surface analysis: A point-count method, *J. Geophys. Res.* 102, 19,293-19,306

Wang A., Haskin L. A., and Cortez, E. (1998) A Raman sensor for *in situ* mineral characterization on planetary surfaces, *Appl. Spec.* 52, 477-487.

Wang, A., Jolliff, B. L., and Haskin, L. A. (1999) Raman spectroscopic characterization of a Martian SNC meteorite – Zagami, *J. Geophys. Res.* 104, 8509-8519.

Abstracts

Wang, A., Jolliff B. L., Haskin, L. A., and Kuebler, K. (1999) Raman spectral features of pyroxene – Application to Martian meteorites Zagami and EETA79001. LPS 1666.

Jolliff, B., Wang, A., Kuebler, K., Haskin, L., and Arvidson, R. (1999) Raman analysis of weathered rocks from the FIDO Mars rover test site, Silver Lake, California. LPS 1512.

Wang, A., Haskin, L. A., and Jolliff, B. L. (1998) Raman spectroscopic study of Martian meteorite and Martian analog, 25th FACCs meeting, Austin, TX, October 1998 (oral presentation given).

Wang A., Cortez E., and Haskin L. A. (1997) A Raman spectroscopic sensor for on-surface planetary remote sensing. *Lunar and Planet. Sci.* 28,

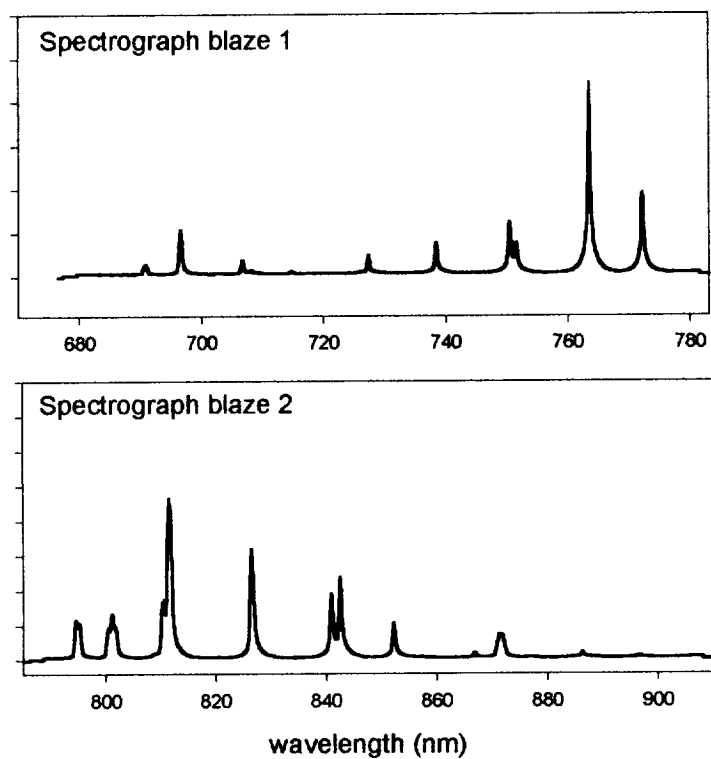
Haskin L. A., Wang A., Jolliff B.L., Korotev R. L., Rockow K. M., and Viskupic K. M. (1997) Laser Raman spectroscopic determination of mineral proportions in rocks on planetary surfaces, *Lunar and Planet. Sci.* 28,

Jolliff B. L., Wang A., and Haskin L. A. (1997) Identification of minerals in several martian analog rocks by Raman spectroscopy, *Lunar and Planet. Sci.* 28,

Wang A., Jolliff B. L., Viskupic K. M., and Haskin L. A. (1997) Raman spectroscopic characterization of different types of pyroxenes. *Lunar and Planet. Sci.* 28,

- Korotev R. L., Wang A., Haskin L. A., and Jolliff B. L. (1998) A Raman point-count study of an Apollo 17 soil. *Lunar and Planet. Sci.* 29.
- Wang A., Haskin L. A., and Jolliff B. L. (1998) Characterization of mineral products of oxidation and hydration by laser Raman spectroscopy – implications for in situ petrologic investigation on the surface of Mars. *Lunar and Planet. Sci.* 29.
- Wang A., Jolliff B. L., and Haskin L. A. (1998) Raman spectroscopic characterization of a highly weathered basalt – igneous mineralogy, alteration products, and a bug. *Lunar and Planet. Sci.* 29.
- Wang A., Jolliff B. L., and Haskin L. A. (1998) Raman spectroscopic characterization of Martian meteorite Zagami. *Lunar and Planet. Sci.* 29.
- Morris R. V., Squyres S. W., Bell J. F. III, Christensen P. H., Economu T., Klingelhöfer G., Hled P., Haskin, L. A., Wang A., Jolliff B. L., and Rieder R. (1998) Analyses of martian surface materials during the Mars Surveyor 2001 mission by the Athena instrument payload. *Lunar and Planet. Sci.* 29.
- Squyres S. W., Arvidson R., Bell J. F. III, Carr M., Christensen P., Des Marais D., Economu T., Gorevan S., Klingelhöfer G., Haskin L., Herkenhoff K., Knoll A., Knudsen J. M., Malin M., McSween H., Morris R., Rieder R., Sims M., Soderblom L., Wänke H., and Wdowiak T. (1998) The Athena Mars rover payload. *Lunar and Planet. Sci.* 29.
- Wang, A., Haskin, L. A., and Jolliff, B. L. (1998) Raman spectroscopic study of Martian meteorite and Martian analog, 25th FACCS meeting, Austin, TX, October 1998 (oral presentation given).
- Wang, A., Jolliff B. L., Haskin, L. A., and Kuebler, K. (1999) Raman spectral features of pyroxene – Application to Martian meteorites Zagami and EETA79001. LPS 1666.
- Wang, A., Jolliff, B. L., Haskin, L. A., and Kuebler, K. E. (2000) Characterization of structures and compositions of quadrilateral pyroxenes by Raman spectroscopy – implications for future planetary exploration, LPS 1875.

Hg spectra obtained by BB1b



double blaze image on CCD

Figure 1. Spectra showing the dual blaze of the grating and the double image of the grating.

Spectral resolution of BB1b

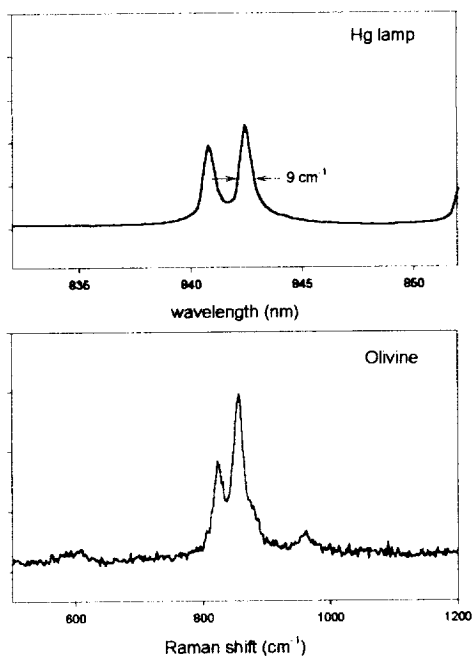
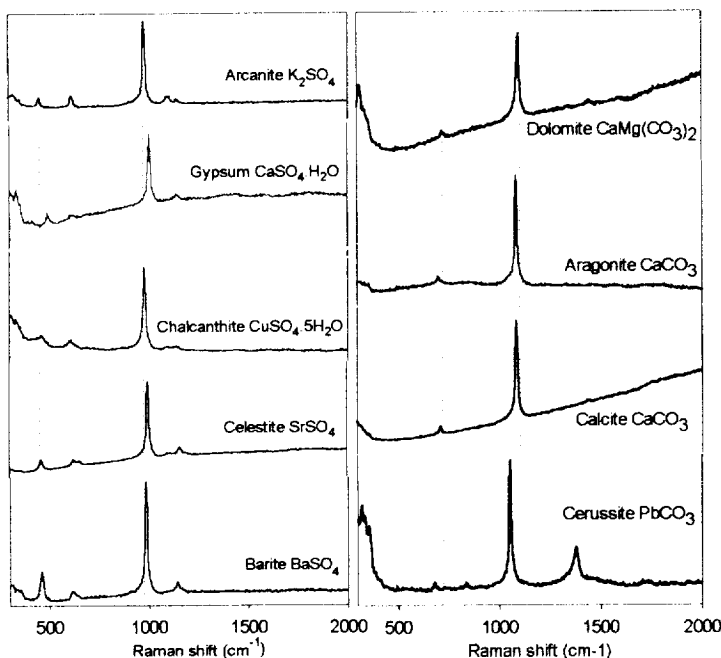


Figure 2 (left). Spectral resolution of the BB1b system.

Figure 3 (below). Spectra of sulfate and carbonate minerals showing that the resolution of breadboard BB1d is good enough that the different minerals can be identified from their peak positions. Spectra of minerals from a terrestrial basalt show that the throughput and resolution of BB1d are satisfactory for determining mineral identities and Mg cation ratios. Engineering Model quality optical components, not yet available at the time of this work, will give improved signal to noise.

b. Spectra of sulfate and carbonate minerals



c. Spectra of major mineral phases in a rock from Ortenburg basalt

